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<b>(54) Title:</b> NON-FLUORESCING OIL-BASED DRILLING FLUID  <b>(57) Abstract</b> <p>The present invention relates to an oil-based drilling fluid, a continuous phase for an oil-based drilling fluid, and additives for an oil-based drilling fluid. The drilling fluid, the continuous phase of the drilling fluid, and the additives for the oil-based drilling fluid are characterized by non-fluorescence when exposed to ultraviolet light. The continuous phase of the drilling fluid is composed of synthetic hydrocarbons selected from the group consisting of branched chain oligomers synthesized from one or more olefins containing a C<sub>2</sub> to C<sub>14</sub> chain length, wherein the oligomers have an average molecular weight of from 120 to 100, and additives. The additives of the continuous phase include surfactants, wetting agents and/or emulsifiers.</p>		

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## NON-FLUORESCING OIL-BASED DRILLING FLUID

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20 This application is a continuation-in-part of commonly assigned, copending patent application U.S. Serial No. 08/004,547 filed January 14, 1993, which is a continuation-in-part of commonly assigned, copending patent application U.S. Serial No. 535,110 filed June 8, 1990, which is a continuation-in-part of U.S. Patent Application Serial No. 503,304 filed March 30, 1990, now abandoned.

25

This invention relates to a non-fluorescing oil-based drilling fluid used in the drilling of subterranean oil and gas wells as well as other drilling fluid applications and drilling procedures. These non-fluorescing drilling fluids are composed of synthetic hydrocarbons, having molecular weights of from 120 to 1000, derived from olefinic monomers and other additives such as surfactants and emulsifiers. The olefinic monomers are from the groups consisting of a carbon chain from  $C_2$  to  $C_{14}$  having at least one polymerizable double bond. The surfactants comprise monounsaturated fatty acids and saturated fatty acids. The emulsifiers comprise saturated fatty acids, saturated amido-amines, and saturated sulfonates. Additional materials that are common to the development and formulation of drilling fluids may

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also be included in the instant drilling fluids provided that the additional materials do not fluoresce in the presence of ultraviolet light.

In rotary drilling there are a variety of functions and characteristics that are expected of a drilling fluid ("drilling mud" or simply "mud"). The drilling fluid is expected to carry cuttings from beneath the bit, transport them up the annulus, and permit their separation at the surface while at the same time the rotary bit is cooled and cleaned. A drilling mud is also intended to reduce friction between the drill string and the sides of the hole while maintaining the stability of uncased sections of the borehole. Likewise the drilling fluid is formulated to prevent unwanted influxes of formation fluids from permeable rocks penetrated and likewise to form a thin, low permeability filter cake which seals pores and other openings and formations penetrated by the bit. Finally, the drilling fluid is used to collect and interpret information available from drill cuttings, cores and electrical logs.

15

Various advantages of using oil-based drilling mud in the rotary drilling of boreholes in the earth have been known for some time. In summary, it can be said that under certain conditions, one or more of the following advantages make oil-based muds more desirable than water-based muds. Lubricity characteristics are excellent. Drilling fluid weighing less than about 8 pounds per gallon can be prepared with an oil-based mud, and have proved advantageous in certain special drilling and coring situations. The penetration of the formation by water is avoided. Cores can be recovered in an *in situ* condition in the presence of hydrous clays and bentonites; no swelling or sloughing is experienced to reduce porosities or cause pipe sticking difficulties. There are fewer problems with hydrophilic shale formations drilled. Evaporite sections such as salt zones can be drilled with minimal leaching of the salt. Furthermore, oil-based muds can be formulated to withstand temperatures up to 500 degrees Fahrenheit.

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On both offshore and inland drilling barges and rigs, drill cuttings are conveyed up the hole by a drilling fluid. With an oil-based drilling fluid, the

cuttings, besides ordinarily containing moisture, are necessarily coated with an adherent film or layer of oily drilling fluid which may penetrate into the interior of each cutting. This is true despite the use of various vibrating screens, mechanical separation devices, and various chemical and washing techniques.

5

Mud logging is a process which involves the recording of information derived from the examination and analysis of formation cuttings. A portion of the drilling fluid is diverted through a gas-detecting device and examined under ultraviolet light to detect the presence of oil or gas. If the drilling fluid fluoresces this indicates that hydrocarbons are present and that the desired formation has been reached.

10

Unfortunately, in most oil-based drilling fluids either the oil used in the fluid or the surfactants that are present naturally fluoresce. This interferes with the results of the mud log because the mud logger cannot accurately ascertain whether formation hydrocarbons are present. This problem has hampered the use of fluoroscopy to determine the presence of hydrocarbon formations when either oil-based or oil-emulsion muds are used.

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Graham et al., U.S. Patent No. 2,951,940, disclose a method of detecting the presence of crude oil in the earth's strata. This method entails contacting the surface of a rock chip that has been carried to the earth's surface by a drilling mud with a reverse-wetting agent. The rock chip is then contacted with ultraviolet light. By comparing the relative fluorescence of the surface of the chip before and after the contacting operation, a positive indication of the presence of the hydrocarbons may be obtained.

25

U.S. Patent No. 3,050,141 discloses a drilling fluid emulsion which comprises an oil- and water-insoluble and immiscible liquid. This liquid is characterized by the fact that it either fails to fluoresce in the presence of ultraviolet light or it fluoresces a different color from typical unrefined hydrocarbons or crude oils. This liquid forms

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a third layer in the presence of oil and water because it is incompatible with both oil and water.

Boyd, U.S. Patent No. 4,787,990 discloses a non-fluorescent oil-based drilling  
5 fluid which consists essentially of branched- and cyclic-paraffins having 11 to 17 carbon atoms per molecule and further having a low aromatic content of less than about 1% and a low normal-paraffin content of less than about 5%.

Mercer et al, U.S. Patent No. 5,096,883 teaches a hydrogenated synthetic  
10 polyalphaolefin having utility as a drilling fluid.

As can be seen from the above, the development of a drilling fluid that exhibits the desirable characteristics of an oil-based fluid and fails to fluoresce in the presence of UV light has long been an unachieved goal of the oil and gas exploration  
15 industry. With the practice of applicant's invention this goal has been realized.

This invention relates to a non-fluorescing oil-based drilling fluid. The drilling fluid is composed of synthetic hydrocarbons that have been synthesized from  
20 one or more olefinic monomers having a chain length of  $C_2$  to  $C_{14}$ . The hydrocarbons have an average molecular weight of from about 120 to about 1000. The drilling fluid also includes surfactants and/or emulsifiers. The drilling fluid is characterized by the fact that it fails to fluoresce in the presence of ultraviolet light.

25 There is no art-accepted definition of non-fluorescence, as virtually all organic molecules will fluoresce to some extent given some excitation source. Typically, oil-based drilling fluids have a natural degree of fluorescence. However, the fluorescent characteristics of the drilling fluids of this invention are below the levels typically encountered or detectable in crude oil and therefore do not confuse the fluorescence  
30 measurement methods and apparatus.

The synthetic hydrocarbon oils of this invention are manufactured by oligomerizing alpha-olefins or other olefins. The resulting oils are mixtures of branched hydrocarbon molecules with carbon numbers that are even multiples of the base olefin. For instance, a synthetic hydrocarbon oil made from C<sub>8</sub> olefins contains  
5 only molecules that are C<sub>8</sub>, C<sub>16</sub>, C<sub>24</sub>, C<sub>32</sub>, etc. These oils can be hydrogenated to achieve complete saturation, or partially hydrogenated, or left unhydrogenated. Preferably they contain no aromatics. Because these oils are synthetic, their molecular size and structure, and their performance characteristics, can be controlled in a predictable and understandable manner.

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The term "surfactant" as used in this application should be understood to include emulsifiers. The terms "surfactant" and "emulsifier" are used interchangeably. The surfactants of the instant invention are fatty acids with one or less points of unsaturation which do not fluoresce in presence of ultraviolet light.  
15 Preferred surfactants are distilled tall oil fatty acids, oleic acid, and isostearic acid.

20

The emulsifiers of the instant invention are derived from monounsaturated or saturated fatty acids, such emulsifiers include amido-amines and sulfonates. Preferred emulsifiers are sorbitan mono- and di-oleates (Arlacel 186 obtained from ICI, Ltd.), amido-amines (Miranol-CS; Rhône-Poulenc), and sulfosuccinates (Emcol-4500; Witco Chemical).

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The drilling fluid may also include other materials common to the development and formulation of drilling fluids provided that the additional materials do not fluoresce in the presence of ultraviolet light. This allows the drilling fluid to be altered to fit specific well conditions. The only requirement is that the drilling fluid must remain non-fluorescent.

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Figure 1 is a three-dimensional representation of an emulsifier that fluoresces in the presence of ultraviolet light. The emulsifier that was utilized in Figure 1 in the oil-based mud is Versamul and it is produced and distributed by M-I Drilling Fluids



Co. This emulsifier is identical to the Kenol-ES emulsifier utilized by Boyd et al. in U.S. Patent No. 4,787,990, column 5, lines 1-15. The sample was diluted to 1:400 prior to testing. This figure was produced by plotting the emission wavelength (x-axis), the excitation wavelength (y-axis) and the maximum intensity (z-axis). The data used to generate this figure may be found in Table 6.

The fluorescence intensity was measured using a Perkin-Elmer (PE) 650-40 fluorescence spectrometer. Additional information concerning this machine may be found in the article by J.M. Brooks et al. entitled "Applications of Total Scanning Fluorescence to Exploration Geochemistry," 15th Annual Offshore Technology Conference, Houston, Texas, May 2-5, 1983, pp. 393-396, OTC 4624, which is hereby incorporated by reference.

Figure 2 is a three-dimensional representation of an emulsifier that does not fluoresce in the presence of ultraviolet light. The emulsifier that was utilized is sold under the brand name Emcol-4500 distributed by Witco Chemical Co. The sample was diluted 1:400 prior to testing. This figure was produced by plotting the emission wavelength (x-axis), the excitation wavelength (y-axis), and the maximum intensity (z-axis). The data used to generate this figure may be found in Table 7. The fluorescence intensity was measured using a Perkin-Elmer (PE) 650-40 fluorescence spectrometer.

Figure 3 is a three-dimensional representation of the fluorescence characteristics of a California oil as it is removed from the ground. This figure was produced by plotting the emission wavelength (x-axis), the excitation wavelength (y-axis), and the maximum intensity (z-axis). The data used to generate this figure may be found in Table 5A.

This invention relates to a non-fluorescing oil-based drilling fluid. For the purposes of this invention, non-fluorescing shall mean that a substance does not fluoresce under ultraviolet light to an extent that is discernable by the naked eye.

More particularly the substance will exhibit a fluorescence intensity of 0 to 800 when diluted 1 to 400. Preferably the substance will exhibit a fluorescence intensity of 0 to 500. This last range of fluorescence is so slight as to be discernable only through the aid of a machine. The following machines may be used to determine the  
5 fluorescence intensity of a substance:

- (1) The Perkin-Elmer (PE) 650-40 fluorescence spectrometer with "SCANR" software programs;
- (2) Oil fluoroscope model 2014 by Alkco services; and
- (3) Mineral light UVS-54 by San Gabriel Products Inc..

10 Additional information concerning the Perkin-Elmer (PE) 650-40 fluorescence spectrometer may be found in the article by J. M. Brooks et al. entitled "Applications of Total Scanning Fluorescence to Exploration Geochemistry." For purposes of this application, the term "non-fluorescence" will be understood to refer to a fluorescence intensity of less than 800 under ultraviolet light when diluted with hexane at a ratio  
15 of 1 to 400.

The drilling fluid is composed of synthetic hydrocarbons that have been synthesized from one or more olefinic monomers having a chain length of  $C_2$  to  $C_{14}$ . The hydrocarbons have an average molecular weight of from about 120 to about  
20 1000. The drilling fluid also includes non-fluorescing surfactants and/or emulsifiers. The drilling fluid is characterized by the fact that it fails to fluoresce in the presence of ultraviolet light.

The following table indicates the preferred olefinic compounds from which the  
25 branched chain oligomeric and polymeric synthetic hydrocarbon can be manufactured.

	<u>Carbon Atoms</u>	<u>Compound</u>
	C <sub>2</sub>	Ethylene
	C <sub>3</sub>	Propene
	C <sub>4</sub>	Butene-1, Isobutene
5	C <sub>5</sub>	Pentene
	C <sub>6</sub>	Hexene
	C <sub>7</sub>	Heptene
	C <sub>8</sub>	Octene
	C <sub>9</sub>	Nonene
10	C <sub>10</sub>	Decene
	C <sub>12</sub>	Dodecene
	C <sub>13</sub>	Tridecene
	C <sub>14</sub>	Tetradecene

Various synthetic hydrocarbons are commercially available to be used in the present invention. For example, polypropenes from AMOCO Chemical Company, product numbers #9009 and 9011; Chevron Chemical Company's product identified as Polymer-560; polybutenes Indopol L-14 and H-15 offered by AMOCO Chemical Company; as well as dimeric, trimeric and tetrameric 1-decenes from Emery, Ethyl and Chevron Corporations are suitable for the present invention. These synthetic hydrocarbons can also be blended to achieve the desired chemical characteristics, which are determined according to the end use of the product.

As identified hereinbefore, the synthetic hydrocarbons that are believed to be useful in the practice of this invention are characterized by chain length and molecular weight parameters. Useful synthetic hydrocarbons are branched chain oligomers synthesized from one or more olefins containing a C<sub>2</sub> to C<sub>14</sub> chain length and wherein the oligomers have an average molecular weight of from 120 to 1000. In the preferred embodiments of this invention the synthetic hydrocarbons are branched chain oligomers synthesized from one or more olefins containing a C<sub>3</sub> to C<sub>12</sub> chain length and wherein the oligomers have an average molecular weight of from 160 to 800. In the most preferred embodiments of this invention the synthetic hydrocarbons are branched chain oligomers synthesized from one or more oligomers containing a C<sub>4</sub> to C<sub>14</sub> chain length and wherein the oligomers have an average molecular weight of 200 to 600.

In each instance the synthetic hydrocarbon mixture must have performance and viscosity characteristics that permit functional utility as a drilling fluid. In its broadest form the synthetic hydrocarbon mixture should have a viscosity of from 1.0 to 6.0 centistokes, preferable a viscosity of from 1.5 to 4.0 centistokes and most preferably from 1.5 to 3.5 centistokes. The synthetic hydrocarbons of the present invention may be hydrogenated (saturated), partially hydrogenated or non-hydrogenated.

The interfacial tension between oil and water is very high, so if the liquids are mixed together they mechanically separate immediately when the agitation ceases, to minimize the interfacial area. Lowering the interfacial tension with a surfactant enables one liquid to form a stable dispersion of fine droplets in the other. The lower the interfacial tension, the smaller the droplets and the more stable the emulsion. In most emulsions, oil is the dispersed phase and water is the continuous phase. However, in "invert emulsions" in which water is the dispersed phase, a suitable emulsion can be formed upon the use of a suitable emulsifier.

Whether an oil-in-water or water-in-oil emulsion is formed depends on the relative solubility of the emulsifier in the two phases. Thus, a preferentially water soluble surfactant, such as sodium oleate, will form an oil-in-water emulsion because it lowers the surface tension on the water side of the oil-water interface, and the interface curves toward the side with the greater surface tension, thereby forming an oil droplet enclosed by water. On the other hand, calcium and magnesium oleates are soluble in oil, but not in water, and thus form water-in-oil emulsions.

An invert water-in-oil emulsion has oil as the continuous phase. The compositions of this invention may comprise 100% oil by volume of the total composition. Water, usually in the form of brine, is normally added in these compositions. Water may be added to the drilling fluid up to a volume of 70%. In more preferred embodiments water is added from 5% to 65% by volume, and in the

most preferred embodiment water is added from 10% to 60% by volume. These brines contain salts such as NaCl and/or  $\text{CaCl}_2$  in varying amounts.

5 The compositions of one embodiment of this invention require emulsifiers to incorporate the brine or water phase into the synthetic hydrocarbon continuous phase. The emulsifiers are chemical compounds which have both oleophilic and hydrophilic parts. The emulsifiers that have demonstrated utility in the emulsions of this invention are saturated or monounsaturated fatty acids, saturated amido-amines, saturated sulfonates, and combinations of the above. Blends of these materials as well  
10 as other emulsifiers can be used for this application provided that the emulsifiers fail to fluoresce in the presence of ultraviolet light. Preferred emulsifiers are oleic acid, isostearic acid, sorbitan monooleate, Miranol-CS, amido-amines, and sulfosuccinates. These emulsifiers are manufactured and distributed by Emery, ICI, Witco, Rhône-Poulenc and M-I Drilling Fluids.

15 Surfactants may also be used in the drilling fluids of this invention. The surfactants that have demonstrated utility in the emulsions of this invention are saturated fatty acids and monounsaturated fatty acids and combinations of the above. Blends of these materials as well as other surfactants may also be utilized provided  
20 that the surfactants do not fluoresce when contacted with ultraviolet light. Preferred surfactants are isostearic acid, oleic acid and Acintol-EPG. These surfactants are manufactured and distributed by the Emery Chemical Co. and the Arizona Chemical Co.

25 The oil-based drilling fluid compositions of this invention may contain an additional chemical known as a wetting agent. Various wetting agents are available and can be included in the compositions. The wetting agents included, but not limited to the present invention, are oxidized fatty acids, saturated fatty acid-based imidazolines. Preferred wetting agents are saturated fatty acid-based imidazolines.  
30 Blends of these materials as well as other wetting agents can be used for this

application provided that the wetting agents fail to fluoresce in the presence of ultraviolet light.

Organophilic clays, normally amine treated clays, are also used as viscosifiers  
5 in the oil-based drilling fluid composition of the present invention. Other viscosifiers, such as oil soluble polymers, polyamide resins, polycarboxylic acids and soaps, can also be used provided the materials are non-fluorescing. The amount of viscosifier used in the composition can vary depending upon the end use of the composition. However, normally about 0.1% to 10% by weight range are sufficient for most  
10 applications. VG-69 is an organoclay material distributed by M-I Drilling Fluids Company.

The drilling fluid composition of this invention may optionally contain a weight material. The quantity depends upon the desired density and viscosity of the  
15 final composition. The preferred weight materials include, but are not limited to, barite, iron oxide, calcium carbonate and the like. The weight material is typically added to result in a drilling fluid density of up to 24 pounds per gallon, preferably up to 18 pounds per gallon and most preferably up to 16.5 pounds per gallon.

20 Finally, fluid loss control agents, such as modified lignite and oil soluble or oil dispersible polymers, can be added to the drilling fluid system of this invention.

The drilling fluid may also include other materials common to the development and formulation of drilling fluids provided that the additional materials do not  
25 fluoresce in the presence of ultraviolet light. This allows the drilling fluid to be altered to fit specific well conditions. The only requirement is that the drilling fluid must remain non-fluorescent.

## EXAMPLES

### Synthesis of Amido-amine 1

96.65 grams of isostearic acid (Emery 871) was added to 20.29 grams of  
5 diethylenetriamine in a mechanically stirred three-neck flask. The reaction mixture  
was heated slowly under nitrogen atmosphere to 450°F. The water formed was  
distilled off. After two hours at 450°F the reaction mixture was cooled to 350°F and  
13 grams of succinic acid was added. The reaction was heated to 390°F for 30  
minutes. The reaction was cooled to 250°F and 37.4 grams of Ethylflow-162  
10 polyalphaolefin was added. The reaction was cooled to 100°F and 13.47 grams of  
methanol was added to the mixture. The resulting product was amido-amine-1.

### Synthesis of Amido-amine-2

In a three-neck flask with a mechanical stirrer, 132 grams of isostearic acid  
15 was added to 47.67 grams of diethylenetriamine. The reaction mixture was slowly  
heated to 450°F and the water from the condensation reaction was distilled off. The  
reaction was kept under nitrogen atmosphere at all times. After 2 hours at 450°F the  
reaction was cooled to room temperature. The resulting product was amido-amine-2.

20 The following are examples of drilling fluid compositions utilizing the  
products of this invention. Where known, the chemical name of each material used  
is supplied the first time the trade name is used.

Synthetic polyalphaolefin Ethylflow-162 was utilized to prepare 14 pounds per  
25 gallon ("ppg"), 80:20 oil:water ratio oil-based mud. Formulation 1 included  
Versacoat and Versawet products which fluoresce in the presence of ultraviolet light,  
while Formulation 2 included products of this invention. Formulation 2 did not  
fluoresce in the presence of ultraviolet light.

Formulation 1 (control)Formulation 2

	158.000g	Ethylflow-162	158.0g	Ethylflow-162
	49.37g	water	49.37g	water
5	17.89g	calcium chloride	17.89g	calcium chloride
	7.5g	Versawet (imidazoline)	7.5g	Emery 871 (isostearic acid)
	5.0g	Versacoat (amido-amine)	4.0g	Miranol-CS (amido-amine)
	2.0g	lime	2.0g	lime
	2.0g	VG-69 (organophilic clay)	2.0g	VG-69 (organophilic clay)
10	3.0g	Versamod (dimer acid)	3.0g	Emersol 1004 (hydrogenated dimer acid)
	327.0g	Barite	327.0g	Barite

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Table 1 summarizes the rheological properties of the above formulations on initial mixing and the after heating at 250°F for 16 hours. These properties were measured at room temperature.

20

Table 1

RPM	Formulation 1 RPM Reading		Formulation 2	
	Initial	Aged	Initial	Aged
600	150	125	140	150
300	82	65	80	89
200	59	45	55	68
25 100	33	25	30	42
6	8	3	7	14
3	6	2	5	12
PV/YP	68/14	60/5	60/20	61/28
gel strength	8/13	3/6	7/13	13/20
30 emulsion stability	841	1102	490	1047

Formulation 3

A 12 ppg non-fluorescent oil-based mud was prepared using Mobil Chemical Co. unhydrogenated polyalphaolefin MCP-1060 and the surfactants of this invention.

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	171.0g	MCP-1060 (unhydrogenated polyalphaolefin)
	55.6g	water
	19.6g	calcium chloride
	7.0g	isostearic acid
5	2.0g	Emersol-1004
	2.0g	VG-69
	2.0g	lime
	2.0g	Miranol-CS
10	229.0g	Barite

Rheologies were taken on initial mixing and after heat aging at 250°F and 300°F for 16 hours and are reported in Table 2.

Table 2

15	RPM	Initial	250°F/16 hours	300°F/16 hours
	600	123	127	108
	300	71	65	57
	200	52	45	40
	100	28	25	24
20	6	5	5	4
	3	4	3	3
	PV/YP	52/19	62/3	51/6
	gel strength	5/11	5/9	5/9
25	emulsion stability	350	300	300

#### Formulations 4 and 5

14 ppg 80:20 oil/water ratio non-fluorescent oil-based muds were prepared using Mobil Chemical Co. MCP-1038 polyalphaolefin and the emulsifiers of this invention.

Formulation 4Formulation 5

	156.22g	MCP-1038 (unhydro- genated polyalphaolefin)	156.22g	MCP-1038
5	47.78g	water	47.78g	water
	17.31g	calcium chloride	17.31g	calcium chloride
	5.0g	amido-amine-1*	5.0g	amido-amine-1*
	4.0g	Acintol-EPG (distilled tall oil)	-	Acintol-EPG
10	-	amido-amine-2*	4.0g	amido-amine-2*
	6.0g	lime	6.0g	lime
	0.75g	Versa SWA (phosphated imidazoline)	0.75g	Versa SWA
	2.0g	VG-69	2.0g	VG-69
15	342.0g	Barite	342.0g	Barite

\* Amido-amine-1 and amido-amine-2 were synthesized from non-fluorescing saturated fatty acids according to the procedures described previously.

20 The rheological properties of these mud formulations were taken initially and after heat aging at 300°F for 16 hours as recorded in Table 3.

Table 3

	RPM	Formulation 4		Formulation 5	
		Initial	Heat Aged	Initial	Heat Aged
25	600	118	102	84	106
	300	69	67	43	59
	200	55	41	28	41
	100	33	24	15	24
	6	10	3	2	3
	3	9	3	1	3
30	PV/YP	49/20	35/22	41/2	47/12
	gel strength	10/20	5/6	2/4	4/5
	emulsion stability	390	400	380	290

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The following 16 ppg oil-based mud formulations were prepared using Ethylflow-162 polyalphaolefin and the surfactants of this invention. Formulations 6, 7 and 8 are detailed in Table 4 and the rheological properties of each recorded in Table 5.

5

Table 4

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	Formulation 6	Formulation 7	Formulation 8
Ethylflow-162	146cc	146cc	146cc
water	44.5g	44.5g	44.5g
calcium chloride	16.14g	16.14g	16.14g
Acintol-EPG	7.5g	7.5g	7.5g
Emcol-4500 (alkyl sulfo-succinate)	0	0	3.0g
Miranol-CS	2.0g	0	0
Arlacel-186 (sorbitan mono- and di-oleate)	0	2.0g	0
lime	2.0g	2.0g	2.0g
VG-69	2.0g	2.0g	2.0g
Barite	463g	463g	463g

Table 5

RPM	Formulation 6		Formulation 7		Formulation 8	
	Initial	Aged	Initial	Aged	Initial	Aged
600	149	194	174	191	176	205
300	86	114	104	111	101	126
200	63	82	80	83	71	96
100	38	49	50	53	42	61
6	11	9	15	19	7	15
3	10	9	12	17	6	13
PV/YP	63/23	80/34	70/34	80/31	75/26	79/47
gel strength	10/15	10/15	12/18	18/30	7/12	17/30
emulsion stability	750	852	638	1225	621	795

Table 5A represents the fluorescence of a California oil as it is removed from the ground. In accordance with this invention, it is important that the oil itself, as demonstrated in Table 5A, have fluorescence characteristics that are different from those of the drilling mud used. Specifically, in accordance with the practice of this invention, it is important that the maximum intensity is less than 800 for the drilling mud used. Thus, as would be anticipated, the maximum intensity is well above 800 for most of the wavelengths shown for the California oil diluted with hexane by a ratio of 1 to 10,000. The cuttings containing the oil were collected on March 24, 1992. Table 7, on the other hand, demonstrates the fluorescence characteristics of a drilling fluid sample using Emcol-4500 as the primary drilling fluid component. It can be seen that at all wavelengths tested, the maximum intensity is well beneath the 800 number required to characterize the material as fluorescent. The fluorescence values of the materials used in Tables 6 and 7 are demonstrated graphically by Figures 1 and 2, respectively.

Table 5A  
California Oil  
Dilution factor 1:10000

	Emission Wavelength	Excitations Wavelength	Maximum Intensity
5	320	290	2520
	340	290	3600
	360	290	2610
	380	300	1560
	400	330	824
10	420	340	504

Table 6  
Versamul  
Dilution factor 1:400

	Emission Wavelength	Excitation Wavelength	Maximum Intensity
15	320	280	383
	340	290	486
	360	310	1110
20	380	310	1730
	400	310	1540
	420	310	1060

Table 7  
Emcol-4500  
Dilution factor 1:400

	Emission Wavelength	Excitation Wavelength	Maximum Intensity
25	320	300	50
30	340	320	52
	360	340	36
	380	310	28
	400	310	22
35	420	370	24

Table 8 shows the total scanning fluorescent of a variety of materials evaluated for use in the process and product of this invention. In the table, the maximum intensity is 3830 for Versacoat at excitation wavelength 320 nm. and the emission wavelength 380 nm. and the ratio R1 is calculated by dividing intensity at emission maximum 360 nm. by intensity at excitation maximum 320 nm. It has been concluded from the data in Table 8 that the materials having a maximum intensity of greater than 800 would be considered fluorescent and therefore not useful in the process and product of this invention. Those materials having a maximum intensity of less than 800 have shown distinct utility and are not considered fluorescent.

Table 8  
Total Scanning Fluorescence

Sample/Trade Name	Dilution Factor	MAX. INT.	EXC. WAVE.	EM WAVE.	R1
EMCOL 4500 (Emery)	1:400	25	310	370	1.15
VERSACOAT (M-I Drilling)	1:400	3830	320	380	15.49
MIRANOL CS (Rhone-Poulenc)	1:400	29	330	370	.67
VERSAMUL (M-I Drilling)	1:400	1730	310	380	0.82
VERSAWET (M-I Drilling)	1:400	3590	320	390	6.71
Stearic Acid	1:500*	4	310	350	0.95
Tall Oil (distilled)	1:400	297	320	390	1.15
Unhydrogenated polyalphaolefin	1:2	596	320	370	0.62
Unhydrogenated polyalphaolefin	1:400	6	270	310	0.44
UNIDYM 12 (Union Camp)	1:500*	478	270	300	0.26

\* - Sample diluted by weight with hexane.

While the invention has been described in the more limited aspects of a preferred embodiment thereof, other embodiments have been suggested and still

others will occur to those skilled in the art upon the reading and understanding of the foregoing specification. It is intended that all such embodiments be included within the scope of this invention as limited only by the appended claims.

## CLAIMS

1. An oil-based drilling fluid characterized by non-fluorescence when exposed to ultraviolet light comprising:
  - (a) a continuous phase comprising a synthetic hydrocarbon, said synthetic hydrocarbon being synthesized from one or more olefinic monomers having a chain length of  $C_2$  to  $C_{14}$ , said synthetic hydrocarbon having an average molecular weight of from about 120 to about 1000; and
  - (b) an additive selected from the group consisting of surfactants, wetting agents, emulsifiers, and combinations thereof.
2. The drilling fluid according to claim 1 wherein said fluid further includes water.
3. The drilling fluid according to claim 1 wherein said drilling fluid contains up to 70% water by volume.
4. The drilling fluid according to claim 1 wherein said synthetic hydrocarbon is selected from the group consisting of oligomers of: ethylene, propene, butene-1, isobutene, hexene, heptene, octene, nonene, decene, dodecene and combinations or derivatives thereof.
5. The drilling fluid according to claim 1 wherein said surfactant is a fatty acid with one or less points of unsaturation.
6. The drilling fluid according to claim 1 wherein said emulsifier is a saturated fatty acid derivative, a saturated amido-amine, or a saturated sulfonate.
7. The drilling fluid according to claim 1 wherein said surfactant is selected from the group consisting of oleic acid, isostearic acid, sorbitan mono-oleate, amido-amines, sulfosuccinates, or combinations thereof.



8. The drilling fluid according to claim 1 wherein said emulsifier is oleic acid, isostearic acid, sorbitan mono-oleate, or a saturated amido-amine.
9. The drilling fluid according to claim 1 wherein said wetting agent is an oxidized fatty acid or a saturated fatty acid-based imidazoline.
10. A continuous phase of an oil-based drilling fluid wherein said continuous phase is characterized by non-fluorescence when exposed to ultraviolet light, said continuous phase comprising:
- (a) a synthetic hydrocarbon, said synthetic hydrocarbon being synthesized from one or more olefinic monomers having a chain length of  $C_2$  to  $C_{14}$ , said synthetic hydrocarbon having an average molecular weight of from about 120 to about 1000; and
  - (b) an additive selected from the group consisting of surfactants, wetting agents, emulsifiers, and combinations thereof.
11. The continuous phase according to claim 10 wherein said synthetic hydrocarbon is selected from the group consisting of oligomers of: ethylene, propene, butene-1, isobutene, hexene, heptene, octene, nonene, decene, dodecene, and combinations or derivatives thereof.
12. The continuous phase according to claim 10 wherein said surfactant is a fatty acid with one or less points of unsaturation.
13. The continuous phase according to claim 10 wherein said emulsifier is a saturated fatty acid derivative, a saturated amido-amine, or a saturated sulfonate.
14. The continuous phase according to claim 10 wherein said surfactant is selected from the group consisting of oleic acid, isostearic acid, sorbitan mono-oleate, amido-amines, sulfosuccinates, or combinations thereof.

15. The continuous phase according to claim 10 wherein said emulsifier is oleic acid, isostearic acid, sorbitan mono-oleate, or a saturated amido-amine.

16. The continuous phase according to claim 10 wherein said wetting agent is an oxidized fatty acid or a saturated fatty acid-based imidazoline.

17. An additive for an oil-based drilling fluid selected from the group consisting of surfactants, emulsifiers, and wetting agents, wherein said additive is characterized by non-fluorescence when exposed to ultraviolet light.

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18. The additive according to claim 17 wherein said additive is a surfactant.

19. The additive according to claim 18 wherein said surfactant is a fatty acid with one or less points of unsaturation.

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20. The additive according to claim 17 wherein said additive is an emulsifier.

21. The additive according to claim 20 wherein said emulsifier is a saturated fatty acid derivative, a saturated amido-amine, or a saturated sulfonate.

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22. The additive according to claim 17 wherein said additive is a wetting agent.

23. The additive according to claim 22 wherein said wetting agent is an oxidized fatty acid or a saturated fatty acid-based imidazoline.

25

24. The additive according to claim 17 wherein said surfactant is selected from the group consisting of oleic acid, isostearic acid, sorbitan mono-oleate, amido-amines, sulfosuccinates, or combinations thereof.

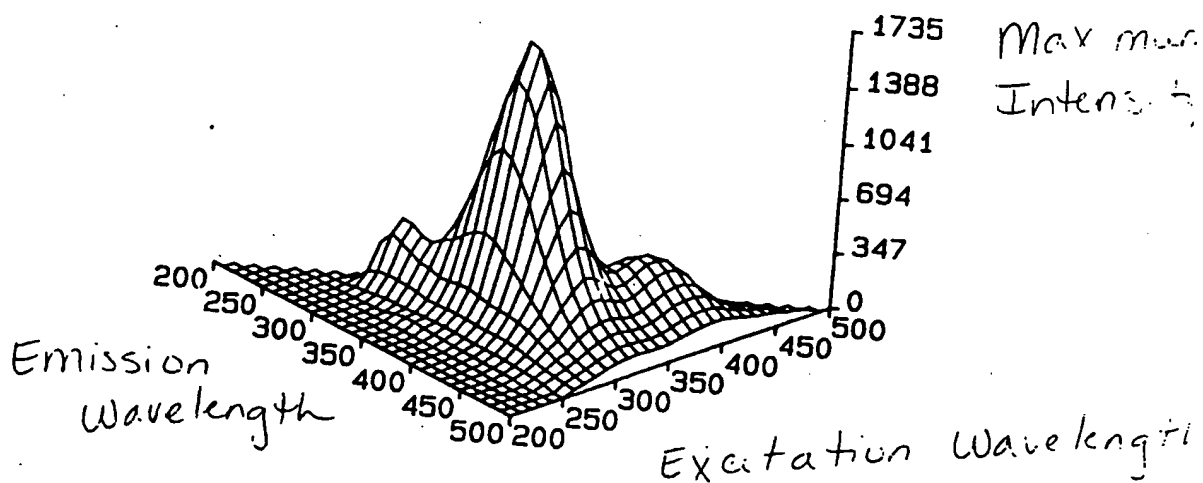
30

25. The additive according to claim 17 wherein said emulsifier is oleic acid, isostearic acid, sorbitan mono-oleate, or a saturated amido-amine.

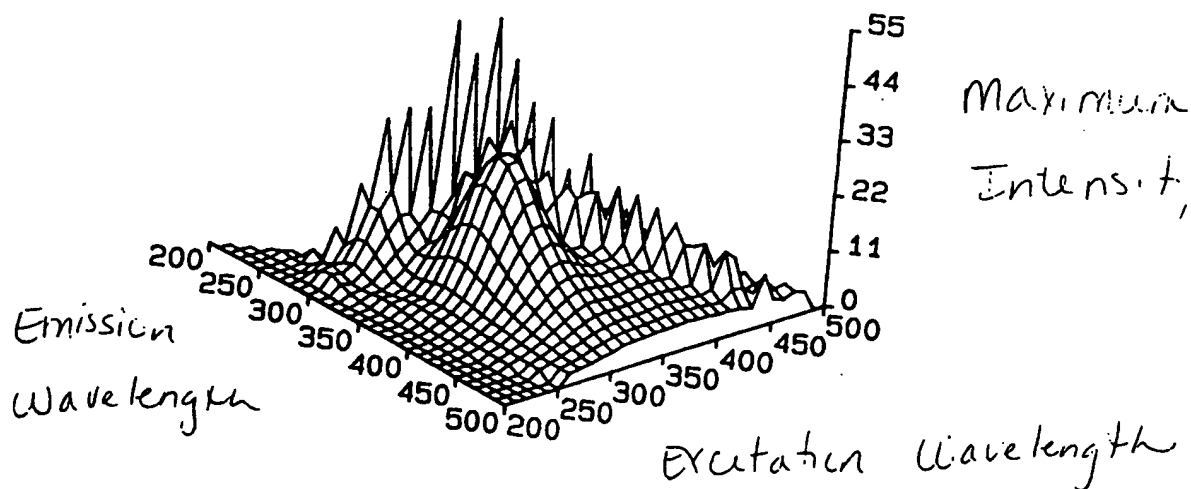
26. The additive according to claim 17 wherein said wetting agent is an oxidized fatty acid or a saturated fatty acid-based imidazoline.

Figure 1

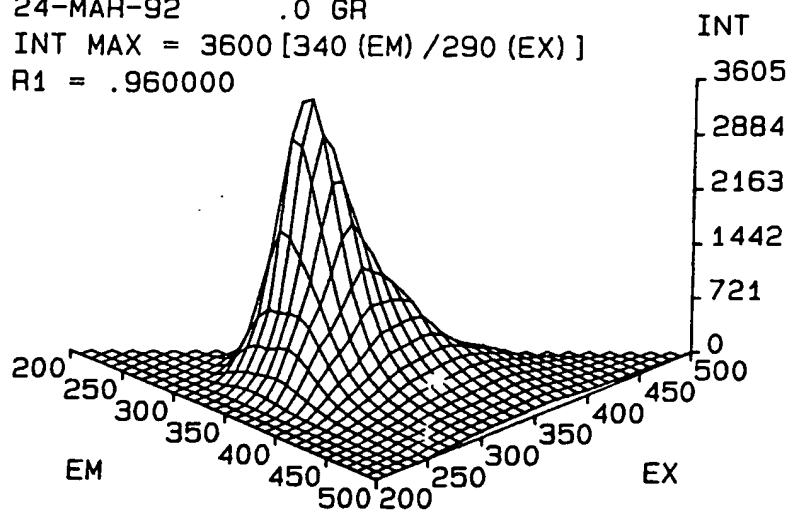
VERSAMUL 1:400  
Dilution factor ~~1:100000~~

Figure 2

EMCOL - 4500  
Dilution factor 1:400



W8926. S2 CALIFORNIA OIL-80 DIL 1: 10000  
24-MAR-92 .0 GR  
INT MAX = 3600 [340 (EM) /290 (EX) ]  
R1 = .960000



T1 = 159927.7

T2 = 153700.5

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/00469

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C09K7/06 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 449 257 (M-I DRILLING FLUIDS COMPANY) 2 October 1991 cited in the application  see page 5, line 46 - page 6, line 15 see page 6, line 55 - page 7, line 27 see page 7, line 50 - page 8, line 18; example 1 ---	1-4,6, 8-11,13, 15-17, 20-23, 25,26
Y	EP,A,0 124 194 (CONOCO INC) 7 November 1984 cited in the application see page 4, line 13 - line 37 see page 13, line 27 - line 37 ---	1-26
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*&\* document member of the same patent family

Date of the actual completion of the international search

18 May 1994

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 94/00469

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP,A,0 325 466 (COASTAL MUD INC) 26 July 1989 see page 2, line 48 - page 3, line 52 ---	1-26
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X	see column 1, line 60 - column 3, line 48 ---	17-26
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information on patent family members

International application No.

PCT/US 94/00469

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